

LASER ABLATION FOURIER TRANSFORM MASS SPECTROMETRIC
INVESTIGATION OF COALS AND RELATED MODEL SUBSTANCES

P.F. Greenwood, H.J. Nakat, G.D. Willett and M.A. Wilson
School of Chemistry, The University of New South Wales,
PO Box 1 Kensington NSW 2033, Australia

and
M.G. Strachan and M.I. Attalla
CSIRO Division of Coal Technology
PO Box 136 North Ryde NSW 2113, Australia

INTRODUCTION

Laser ablation Fourier transform mass spectrometry (LA/FTMS) is a technique which allows the investigation of high molecular weight involatile materials. Coals and cokes represent a class of such materials and in general, mass spectrometric analyses of such carbonaceous materials have generally been restricted to thermal desorption gas chromatography-mass spectrometry. Batts and Batts [1] have recently reviewed the application of mass spectrometry to coal analysis.

The use of pulsed high power lasers in mass spectrometry as a soft ionization technique is now well established and has facilitated the investigation of macromolecular species of several thousand mass units [2]. The pulsed nature of the Fourier transform mass spectrometer and high powered pulsed IR or UV lasers represents a logical combination for laser ablation experiments. This technique offers several advantages [2-4], the most important of which are high mass resolution and extended mass range, over other mass spectrometric methods which incorporate time-of-flight or deflection type analysers and other 'soft ionization' techniques.

The carbon content of coal directly reflects its rank and level of maturity. During coalification, the terrestrial organic matter is modified by geochemical processes to ultimately form anthracitic coals. Particularly significant is the transition observed at about 89% carbon content where aromatic lamellae in the coal begin to condense to form polycyclic aromatic compounds. These polynuclear species are important components of anthracitic coals where they form the basis for the further growth of graphite sheets.

In this study, we have examined by FTMS different rank coals and model systems. The latter include graphite and different ring size polynuclear aromatic hydrocarbons. The ionization mechanisms and the effects of irradiance conditions have also been examined.

EXPERIMENTAL

Table 1 presents the maceral compositions and elemental analyses data for the coal samples studied. These included two American anthracitic coals, obtained from the Pennsylvania State University sample bank, and an Australian semi-anthracitic coal and lignite. The graphite and individual polynuclear aromatic compounds were obtained from commercial sources, and were of such purity to be used as received.

The mass spectra were obtained using a Bruker CMS-47 FT/ICR mass spectrometer equipped with a 4.7T superconducting magnet and a 24 bit/256 kW Bruker ASPECT 3000 computer. The stainless steel high vacuum chamber and direct insertion probe were evacuated by Baisers 330 lsec⁻¹ and 50 lsec⁻¹ turbo molecular pumps, respectively. For the laser ablation experiments, the samples were finely powdered together with NaCl and pressed into a detachable cylindrical stainless steel satellite probe tip. This in turn was inserted, using a Bruker direct insertion probe, into a titanium single section cylindrical (r=30 mm, h=60 mm) ICR cell.

A typical laser ablation experiment involved focussing the laser beam (1064 nm, Spectra Physics DCR-11) of a Nd-YAG laser to 0.1 mm at the sample satellite probe tip. The sample surface was subjected to laser beam irradiances in the range of $0.005\text{--}1000\text{ MWcm}^{-2}$, with reproducible irradiance variations being obtained by using neutral density filters. Two laser irradiance times were used in the experiments, corresponding to a long pulse mode (230 μs) and a Q-switched mode (8 nsec). Through careful regulation of the laser irradiance near the ionization threshold it was possible to monitor the effect of laser irradiance on the resulting mass spectra. A normal pulse sequence consisted of the laser irradiation followed by a 1 second delay, prior to data acquisition to allow the desorbed neutral species to be evacuated and the pressure to return to $1\text{--}10^{-8}$ mbar. Ions were trapped in the cell by potentials of approximately 4V. The transient was stored as 64 k data points prior to Fourier transformation to obtain a magnitude mode spectrum. For the results reported here, no attempt was made to improve resolution of the high mass carbon clusters by selecting smaller mass ranges, to improve the density of data points.

RESULTS AND DISCUSSION

Model Systems

Figure 1 shows the mass spectra of two of the polynuclear aromatic hydrocarbon compounds; chrysene and fluoranthene. The most abundant ions in each spectra result from the molecular ion, M^{+} , and the adduct ion $[M + X]^{+}$, where X is Na^{+} . This ion distribution was found for all the polynuclear aromatic model compounds, for the laser ablation experiments. This result indicates the occurrence of at least two different ionization pathways. The presence of adduct ions in the mass spectra indicates a surface laser desorption mechanism, with attachment of alkali metal ions to involatile molecules [5]. For example, in Figure 1(a) the adduction of chrysene, $[\text{C}_{18}\text{H}_{12} + \text{Na}]^{+}$ (m/z 251) results from the attachment of Na^{+} to the aromatic compound to form the ionized species, with subsequent volatilization by laser desorption.

In contrast, there is no information to allow a confident prediction of the M^{+} molecular ion formation mechanism. It could be a laser desorption process, where simultaneous ionization and vaporization of the condensed phase leads to the formation of the M^{+} ions. Alternatively, a multiphoton ionization mechanism where neutrals, which are desorbed by the initial part of the laser pulse, are ionised by photons in the latter part of the laser pulse may be occurring. Yet another possibility is ion/molecule reactions, where smaller desorbed species recombine in the emitted plasma cloud. However, the important point to note is that there is more than one ion formation mechanism possible [6] and it is unlikely in any high power laser ablation experiment that all ions are formed by a single ionization process. Considering the uncertainty concerning these ionization mechanisms for M^{+} formation, it appears that laser desorption ionization of involatile surface species may only be unequivocally assigned from adduct ions.

Interestingly, laser ablation of the graphite sample (Figure 2(a)) at similar irradiation conditions as the model compounds gave only M^{+} spectra. The mass distribution observed for the carbon cluster ions ranged from C_{11}^{+} to C_{28}^{+} , with the most intense ions at C_{15}^{+} and C_{19}^{+} . Laser ablation FTMS studies on graphite have been previously reported by McElvany *et al.* [7], who observed carbon clusters upto C_{180}^{+} , with the most stable species being C_{60}^{+} . Compared with the present study, this earlier investigation used (1) a different instrument configuration, (2) different irradiation conditions, and (3) ejected all species below C_{18}^{+} to enhance the resolution of the higher molecular weight carbon clusters. It has also recently been reported that C_{60}^{+} is remarkably stable and is, in fact, a spherical aromatic molecule with a truncated icosahedron (soccer ball) structure. Indeed, carbon clusters have been proposed as being important as nucleation agents for soot formation and being present in interstellar dust clouds [8].

The absence of $[M + Na]^+$ adduct ions in the mass spectrum means that it is difficult to determine, unequivocally, whether the carbon cluster ions are formed from surface species by simple volatilization and photodissociation (i.e. a laser desorption process) or are formed in the gas phase by the other ionization mechanisms, the latter of these being more likely [7]. It is also possible in laser desorption experiments that the adduct ions are not observed, as very large aromatic species may not necessarily form stable adducts with Na^+ .

Negative ion carbon clusters have also been observed for the graphite sample (Figure 2(b)), with the largest cluster being at C_{25}^- (m/z 300). The detection of negative ions is easily performed in the FTMS by reversing the polarity of the trapping plate potentials. The negative ion carbon cluster distribution does not resemble that of the cations. Only smaller carbon cluster anions are stable. The difference between the anion and cation clusters can be attributed to a different mechanism of formation. The emitted plasma cloud is made up of ions, neutrals and electrons, and electron attachment is believed to be the mechanism of formation for the anionic clusters. It is reported that these carbon cluster anions do not undergo reaction with neutral carbon species in the plasma to form larger carbon clusters ($>C_{30}$) [7].

Coals

Laser ablation of all the anthracitic coals only generated charged carbon clusters. There was no evidence of adduct ion formation in the mass spectra, even when the samples were heavily doped (i.e. 20:1) with alkali metal salts. Figure 3(a&b) shows the mass distributions for the cationic (C_n^+ where $3n < 150$) and anionic (C_n^- where $2n < 25$) carbon clusters from the Australian anthracitic coal. The mass distributions are typical of those also observed for the two American anthracitic coals. In all cases, the most intense and stable cationic carbon cluster was C_{60}^+ , and the mass distributions were similar to those previously reported for graphite [7].

It is also evident from figure 3(a) that the even numbered clusters have greatest stability, and Smalley et al. [9] have proposed a likely formation mechanism to account for this phenomenon. Formation of the high even mass carbon cluster cations has been attributed to ion/molecule reactions that occur in the laser desorbed plasma. Highly reactive carbon radicals ranging in size from one to twenty atoms are initially desorbed from the sample. These then react with each other to form the larger more stable even numbered clusters.

The mass distribution of the anionic carbon clusters (Figure 3(c)) is similar to that observed from the graphite sample. It would, therefore, appear the same mechanism as that proposed for graphite [7] also accounts for the low mass range distributions from the three anthracitic coals.

Another important factor which has been observed to influence the laser ablation mass spectra is the laser irradiance time. Figures 3(a&b) and (c&d) show the effect of different laser irradiance times (200 μ s) and 8 ns) on the mass distributions of the cationic and anionic carbon clusters, respectively. It is believed that both the laser irradiance time and the molecular structure of the sample are important in determining the formation and mass distribution of the carbon clusters [7]. This is dramatically shown in the mass distributions of the cationic carbon clusters. The mass distribution produced at an irradiance time of 200 μ s (Figure 3(d)) shows species up to C_{150}^+ , while that produced with an irradiance time of 8 ns (Figure 3(b)) shows only a few lower mass range carbon clusters. In contrast, the mass distributions of the anionic carbon clusters (Figures 3(c&d)) show only a small variation with different irradiance times.

The mass distributions from the laser ablation experiments on the lignite (Figures 4 (a&b)) are similar to those from the anthracitic coals. Again, the most intense and stable species in the mass distribution of the cationic carbon clusters, which range up to C_{150}^+ , is C_{60}^+ . Similarly, the mass distribution of

the anionic carbon clusters are, again also, below C_{25}^- . Apparently, the mechanisms which generate the cationic and anionic carbon clusters from the graphite and the anthracitic coals are the same as those forming ionic carbon clusters from the lignite.

The irradiation conditions used in our laser ablation experiments did not produce large (i.e. $n > 30$) carbon clusters from the graphite. However, no difficulty was encountered in generating these species from either the anthracitic coals or lignite. This observation suggests that more energy is required to break the highly ordered and strongly bonded covalent graphite lattice, than the structural components and linkages in coals.

CONCLUSIONS

1. A study of polynuclear aromatic hydrocarbons by FTMS has shown the viability of the technique for investigating surface species.
2. Cationic and anionic carbon clusters are generated from anthracitic coals and lignite.
3. Under the experimental conditions used in this investigation, the mass distributions of the cationic and anionic carbon clusters appear to be independent of coal rank, and similar to those previously reported for graphite.
4. The absence of $[M+Na]^+$ adducts in the mass distributions from the coals means that the carbon clusters cannot be unequivocally considered as being desorbed from the coal surface, but more likely are formed in the gas phase by alternate ionization mechanisms.
5. The formation and mass distributions of the cationic carbon clusters are dependent on the laser irradiation time.
6. The potential of FTMS for studying carbonaceous materials, such as coals and graphite, has been demonstrated. Further developments in the technique should provide greater insight into the structure and nature of these materials.

REFERENCES

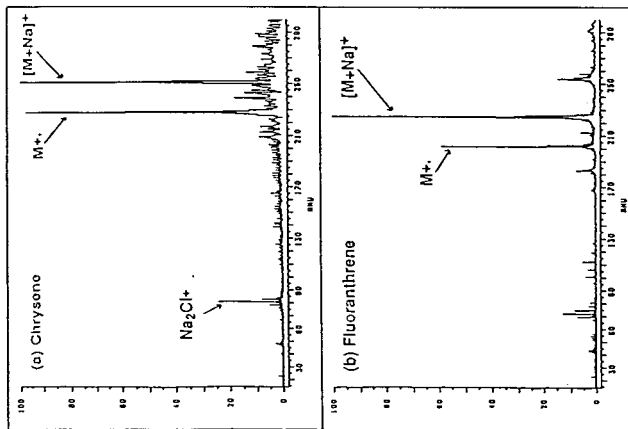
1. B.D. Batts and J.E. Batts in *Spectroscopic Analysis of Coal Liquids*, (Ed. J.R. Kershaw), Elsevier, (1989), 61-125.
2. D.H. Russell, *Mass Spec. Rev.* 5, 167 (1986).
3. A.L. Burlingame, D. Maltby, D.H. Russell and R.T. Holland, *Anal. Chem.* 60, 294R (1986).
4. R.B. Brown, D.A. Weil and C.L. Wilkins, *J. Macromol.* 19, 1255 (1986).
5. C. McNeal, *Anal. Chem.* 54, 43A (1982).
6. R.J. Cotter, *Anal. Chem.*, 56, 485A (1984).
7. S.W. McElvany, H.H. Nelson, A.P. Baronvaski, C.H. Watson and J.R. Eyler, *Chem. Phys. Letts.* 134, 214 (1987).
8. R.M. Baum, *Chemical and Engineering News*, Aug. 29, 1988, 33-35.
9. Q.L. Zhang, S.C. O'Brien, J.R. Heath, Y. Liu, R.F. Curl, H.W. Kroto and R.E. Smalley, *J. Phys. Chem.*, 90, 525 (1986).

TABLE 1 Geochemical data on coal samples

Sample ^A Identif- ication	Seam	State/Country	Rank	Maceral Composition (%)		Elemental Composition (%)				
				Vitrinite	Inertinite	C	H	N	O ^B	S
PSOC 628	Penna No.2	Pennsylvania/ USA	Anthracite	92	8	0	94.9 ^C	3.4	1.0	0.1 0.6
PSOC 867	Primrose	Pennsylvania/ USA	Anthracite	78	22	0	96.9 ^C	1.0	0.8	0.7 0.6
	Yarrabee	Queensland/ Australia	Semi- anthracite	41	59	0	90.5 ^D	3.7	1.8	3.3 0.7
	Loy Yang	Victoria/ Australia	Lignite	95	2	3	69.2 ^D	4.9	0.9	25.0 0.3

A - Pennsylvania State University sample bank; B - by difference; C - Analysis determined on a dry, mineral-matter-free basis; D - Analysis determined on a dry, ash-free basis

INFRARED LASER ABLATION OF CHRYSENE AND FLUORANTHRENE



INFRARED LASER ABLATION OF GRAPHITE

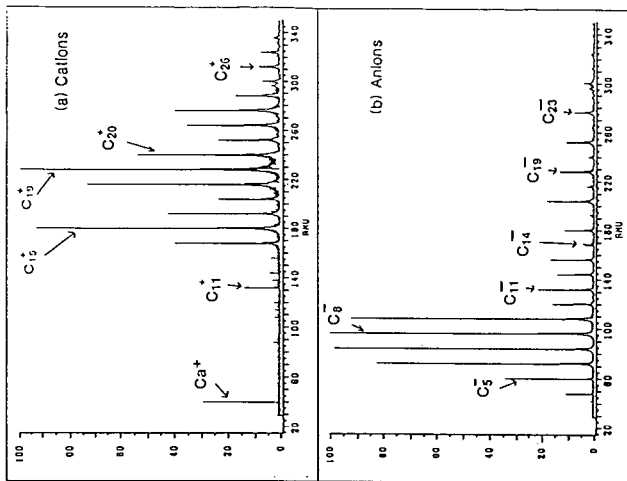


Fig. 2. (a) Positive and (b) negative ion laser ablation FT-mass spectra of graphite at 70 KW/cm² with an irradiance time of 200 μ s.

Fig. 1. Positive ion laser ablation FT-mass spectra of the model compounds (doped with 1:1 NaCl) (a) Chrysene and (b) Fluoranthene at 1600 MW/cm² with an irradiance time of 8 ns.

INFRARED LASER ABLATION OF AUSTRALIAN LIGNITE

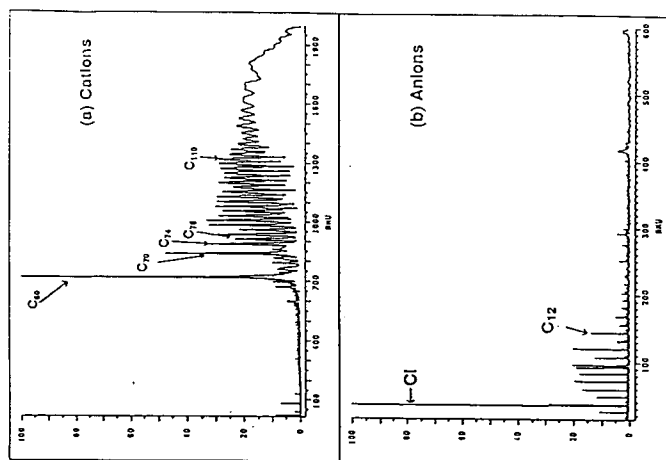


Fig. 4. (a) Positive and (b) negative ion laser ablation FT-mass spectra of an Australian lignite (doped with 1:1 NaCl) at 15 kW/cm² and 30 MW/cm² and an irradiance time of 200 μ s and 8 ns respectively.

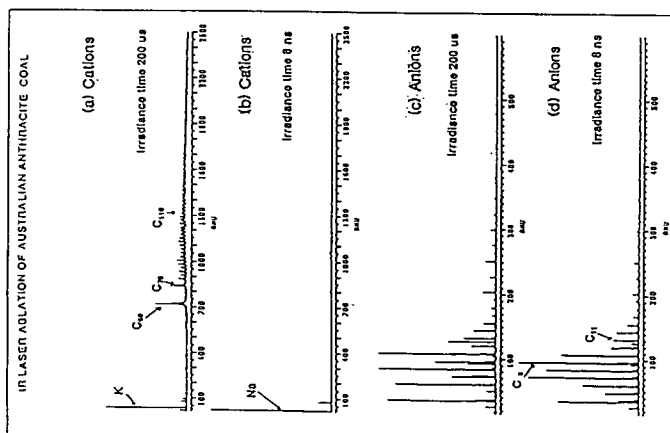


Fig. 3. (a-b) Positive and (c-d) negative ion laser ablation FT-mass spectra of an Australian anthracite coal (doped with 1:1 NaCl) at 15 kW/cm², 10 MW/cm², 70 kW/cm² and 30 MW/cm² respectively.